

Differentiating between physical and chemical constraints on pesticide and water movement into and out of soil aggregates

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Abstract: A laboratory experiment comparing the movement of $^3\text{H}_2\text{O}$ and [^{14}C]isoproturon into and release from soil aggregates is described. Small aggregates (2.0–2.4 mm) were prepared from a clay topsoil and maintained at three different initial moisture conditions. A small volume of the radioisotope solution was introduced prior to bathing the aggregates in a 2 mM CaCl_2 solution to represent new rainwater. Whilst the $^3\text{H}_2\text{O}$ was imbibed by the air-dry aggregates, the pesticide did not follow the water but remained on the surface of the aggregates. This may be related to its sorptive properties and an excess of sorption sites on the sorbent with respect to the sorbate. Increasing the length of exposure of the moist aggregates to [^{14}C]isoproturon reduced the initial release of the compound into the bathing solution, probably due to diffusion (retarded by sorption) into the aggregates. The diffusion model described by Crank and a non-equilibrium desorption model were used to analyse the $^3\text{H}_2\text{O}$ and [^{14}C]isoproturon release curves. This showed that the release of $^3\text{H}_2\text{O}$ from the dry aggregates was controlled by diffusion. The release of isoproturon was probably controlled by non-equilibrium sorption/desorption from air-dry aggregates and by a combination of non-equilibrium sorption/desorption and diffusion from wet aggregates.

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1 INTRODUCTION

When it rains the top layer of the soil plays a critical role in controlling the release of pesticides for transport to other parts of the soil or drainage system. A wide variety of factors have been identified which are likely to be important in the release and transport of pesticides. These include soil structure, soil-water antecedent conditions, meteorological conditions and the sorptive behaviour of the pesticide.^{1,2} The interactions between these different factors and their effects are as yet poorly understood.

In structured soils which exhibit preferential flow characteristics, an important feature (particularly where clay minerals are present) is the presence of soil aggregates in the topsoil. The properties of soil aggregates are associated with the parent material and organic matter content which helps to give them their stability. Their size may vary from <4 mm to many cm in diameter. They may be formed by a combination of the cultivation practice followed by the weathering processes of shrinkage and freeze-thaw.³ Between the aggregates are the mesopores and within the aggregates are the much smaller diameter micropores which are a reflection of the soil type.⁴ The relationship

between these intra-aggregate micropores, mesopores and larger inter-aggregate macropores has a large influence on solute release and transport. Via diffusion or convection, the applied pesticide may move onto and into the aggregates, depending on the antecedent moisture conditions. An important question is how the location of pesticides on or within these aggregates may affect their mobilisation by new storm water.

It might be expected that pesticides that enter the micropores within a soil aggregate would be less accessible to storm water running through the soil than are pesticides on aggregate surfaces. Micropores within an aggregate have been categorised as being either within the dynamic (at the surface) or stagnant region with respect to flowing macropores.^{5,6} It is possible that some of the micropores within an aggregate are extremely inaccessible, such that any solute that does enter could be considered as physically entrapped and unlikely to be transported unless the aggregate is broken up.⁷

It might be predicted that if a pesticide is applied to a structured soil where some drying of the surface layer has taken place, less may subsequently be available for transport processes than when an application is made

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to a soil close to field capacity. Subsequent light rainfall might cause pesticide and water to be imbibed into the aggregates. This would then reduce their accessibility to mixing with new storm water. Besides the described physical factors, adsorption/desorption processes control the release of pesticides from soil aggregates into the soil solution and thus their availability for transport in preferential flow events.

The aim of this work was to employ simple techniques to distinguish between the physical and chemical restraints on pesticide release from soil aggregates. Tritiated water has been used previously to characterise the movement of water in soil.⁸ In this case, small quantities of [¹⁴C]isoproturon were added together with ³H₂O to the aggregates to trace the behaviour of the pesticide in comparison with water. Soil aggregates at different moisture contents were used to represent different antecedent conditions. The aggregates were then bathed in a calcium chloride solution to mimic the aggregates being exposed to storm water. The release of the different radioisotopes from the aggregates into the bathing water was then monitored.

2 MATERIALS AND METHODS

2.1 Soil aggregates

The soil used in this study was obtained from Oxford University Farm, Wytham from a field site that has been used to study the fate, behaviour and transport of the herbicide isoproturon in a heavy clay soil of the Denchworth series.⁹ At the field site, the Ap horizon (0–26 cm) had a clay content of 57%, a pH of 7.8 and an organic carbon content of 3.1%. Due to the small pore diameter of the clay soil matrix, water can move through the matrix only at a very slow rate. In winter, under normal rainfall conditions, the topsoil soon becomes saturated. Under these conditions by-pass flow is the dominant mechanism for water and pesticide movement to the drainage system can lead to high concentrations in receiving streams.^{10,11} To make farming, and in particular the growing of winter cereals, viable on these soils, the installation of a drainage system with mole drains is advised. At least 18% of the soils, in agricultural use in England and Wales are in this category (Beard GR, pers comm).

Soil was collected from the top 2 cm of the surface and air dried, ground with a pestle and mortar to break up the larger aggregates and then passed through a sequence of sieves. The air-dried samples contained 4% moisture by weight. The fraction used in the experiment was 2.0–2.4 mm and was stored open at room temperature for six months, prior to use.

Soil moisture adjustments were then made by adding the required amount (by weight) of 2 mM calcium chloride solution to 1.0 g of air-dry soil (fresh weight; actual weight 0.96 g soil to 0.04 g water). This solution was added evenly to the aggregates with a micro-pipette. The soil aggregates were accurately

weighed into plastic 30-ml disposable containers (Sterilin). Three moisture contents were chosen:

- (1) Air-dry (4% moisture content) aggregates: no CaCl₂ solution added.
- (2) 19% moisture content aggregates: 0.15 ml of CaCl₂ solution added per 1 g of air-dry soil.
- (3) 34% moisture content aggregates: 0.30 ml of CaCl₂ solution added per 1 g of air-dry soil.

As the highest moisture content by weight of the soil recorded during the winter period was 33%, this last treatment was considered to saturate the aggregates. All of the solution was held within the aggregates. After each soil sample had been adjusted to its required moisture content, the containers were sealed and the samples left to equilibrate, at 4 °C, for 13 days.

2.2 Pesticide and tracer application

Isoproturon (3-(4-isopropylphenyl)-1,1-dimethyl-urea) is a non-ionic, substituted urea herbicide. It is applied pre- or post-emergence to control annual grasses and broad-leaved weeds in barley, rye and wheat. A filter-sterilized stock solution of unlabelled isoproturon in water (33.5 µg ml⁻¹), was prepared and stored at 4 °C in the dark prior to use (all the radioisotope solutions were stored under the same conditions). The solution for spiking the aggregates was formulated to apply 1 µg of isoproturon to 1 g (1 mg kg⁻¹) dry weight of soil in a 40 µl application volume. Each 40 µl volume contained 100 ng of [¹⁴C]isoproturon (887 MBq mmole⁻¹) with the remaining 900 ng of isoproturon required to achieve the 1 mg kg⁻¹ application rate provided from the unlabelled isoproturon stock solution. The spiking solution also contained tritiated water (18.5 MBq per 500 µl) at a concentration that ensured approximately 30 000 dpm (0.5 kBq) of ³H was present in each 40 µl application.

From the prepared spiking solution, 40 µl aliquots were evenly applied over the surface of the aggregates (excluding a soil blank) using a micro-pipette.

2.3 Exposure of the aggregates to the radioisotope solution and sampling

The experiment had one soil aggregate size (2–2.4 mm) with three initial moisture contents (4, 19 and 34% by weight). After [¹⁴C]isoproturon and ³H₂O were applied to each set of aggregates they were allowed to equilibrate for 1, 2, 4 and 24 h before addition of 10 ml of 2 mM CaCl₂ bathing solution. Three replicates were used for each equilibration time. After the addition of the bathing solution, each sample was gently swirled, then left to settle at room temperature (21–22 °C) before being sampled at time intervals of 30, 60, 90, 180 and 1440 min after bathing.

2.4 Analysis

At each sampling, duplicate aliquots (0.5 ml) of bathing solution were removed by pipette and mixed with 5 ml of Ultima Gold scintillant (Canberra

Packard, Pangbourne, Berks, UK) in 10-ml polyethylene scintillation vials. A Beckman LS 6500 multi-purpose scintillation counter (Beckman Instruments (UK) Ltd, High Wycombe, Bucks) was set up to analyse samples for ^{14}C and ^3H concurrently. Each sample was counted twice for five minutes against duplicate control (background) samples so that the background radiation levels could be automatically subtracted. The scintillation counter possessed a quench monitor which determined the extent of quench in the sample. Automatic quench correction adjusted the window settings as a function of quench. The results were expressed as disintegrations per minute (dpm). Previous assessments of isoproturon degradation in this soil gave half-lives in the order of 18 days, suggesting that over a 24-h incubation losses would only be 2–3%.¹²

3 RESULTS AND DISCUSSION

The aggregates appeared to remain stable through all the stages of the experiment. Figures 1a and 1b show the release of the radioisotopes into the bathing solution after 1 h and 24 h equilibration respectively. Similar release patterns were observed with the aggregates which had been allowed to equilibrate for 2 and 4 h (data not shown). As described earlier, the bathing solution represented new storm water which floods the topsoil mixing zone during a rainstorm. The aggregates are distinguished from one another by the different initial moisture contents. Close to 100% of the $^3\text{H}_2\text{O}$ could be recovered from the bathing solution in each of the treatments. In contrast, no more than 74% of the [^{14}C]isoproturon could be recovered in the bathing solution after 24 h from the different treatments. The different behaviour of the two radioisotopes reflects the sorptive potential of an organic chemical. In the first few hours of bathing the aggregates, no more than 30–40% of the [^{14}C]isoproturon entered the bathing solution. This suggests that equilibrium between [^{14}C]isoproturon on the aggregates (aqueous or solid phase) and that in the bathing solution was not reached within the first four hours. This implies that for a short rainfall event (2–3 h), less isoproturon may be mobilized than expected.

The initial aggregate moisture contents of 19 and 34% had no effect on the release of the previously applied $^3\text{H}_2\text{O}$ (Figs 1a and 1b). However, release of $^3\text{H}_2\text{O}$ applied to the air-dry aggregates into the bathing solution was delayed consistently in each of the different durations of exposures (Figs 1a and 1b), this difference occurring only in the first 3 h after addition of the bathing solution. This implies that the labeled water had been imbibed into the micropores within the dry aggregates, in agreement with earlier studies.³ Thus, the initial low recovery of $^3\text{H}_2\text{O}$ was probably due to the delay involved in $^3\text{H}_2\text{O}$ diffusing out of the small pores inside the aggregate and into the bathing solution. Also, perhaps when the dry aggregates were re-saturated with the bathing solution, the rapid

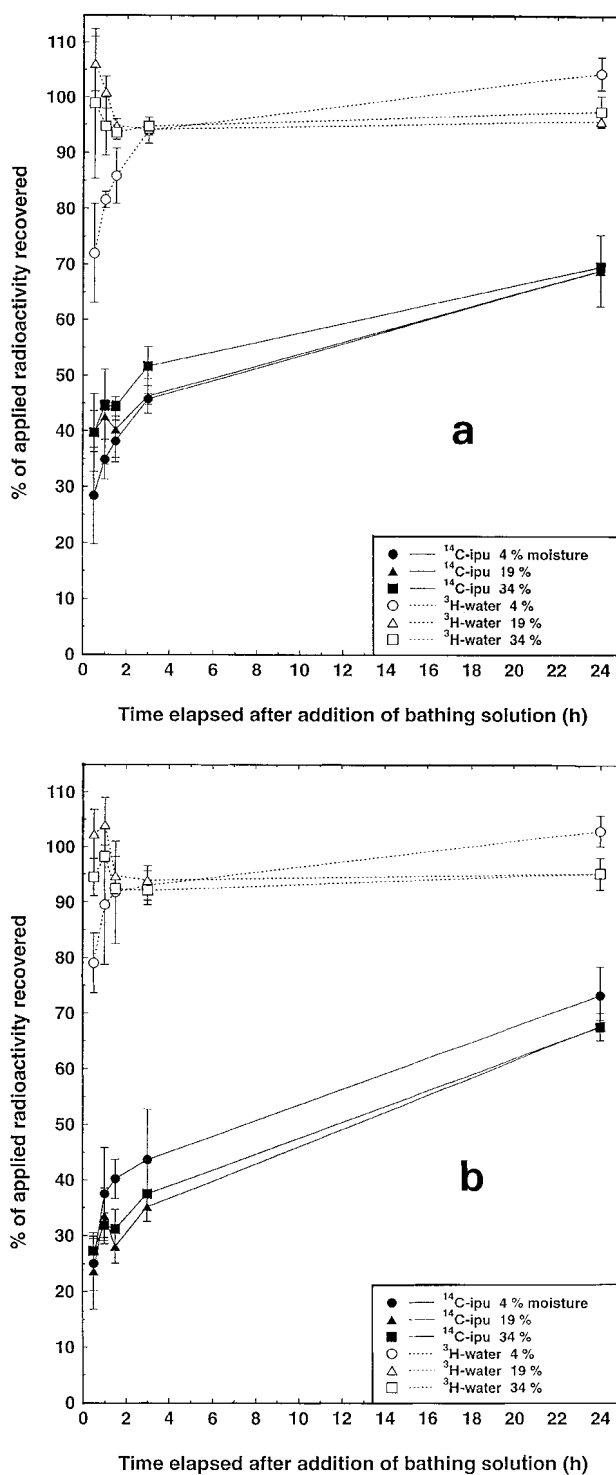


Figure 1. Recovery of [^{14}C]isoproturon (ipu) and $^3\text{H}_2\text{O}$ from aggregates after (a) 1 h and (b) 24 h equilibration (mean of three replicates with standard deviation shown).

movement of water into the aggregate would initially delay the recovery of the $^3\text{H}_2\text{O}$ from inside the aggregates. It is probable that the larger the diameter of the aggregate, the greater would have been the delay.¹

Contrary to expectations, the initial moisture content of the aggregates (from air-dry to saturated) had

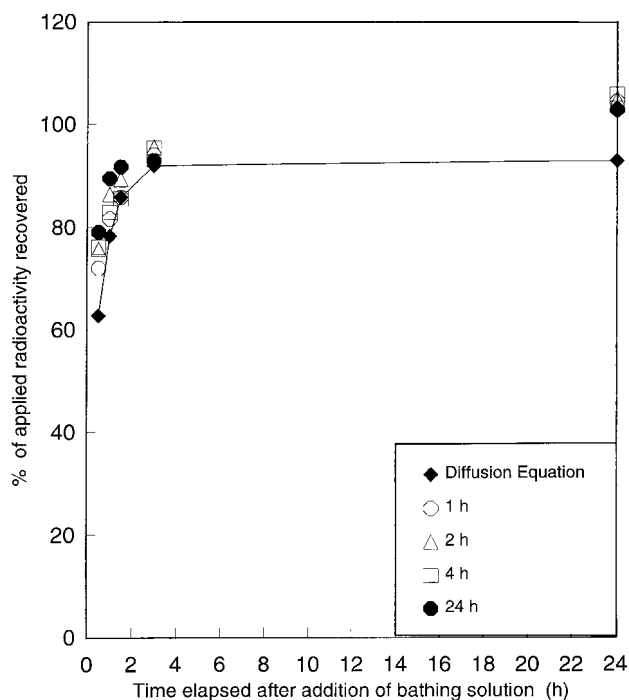


Figure 2. Recovery of $^3\text{H}_2\text{O}$ from the 4% water content aggregates after 1, 2, 4 and 24 h equilibration compared with that estimated from diffusion theory.

no effect on the release of the previously applied [^{14}C]isoproturon (Figs 1a and 1b). As the release of [^{14}C]isoproturon was independent of each aggregate moisture content, the association of applied [^{14}C]isoproturon with the aggregates appeared to be only at the surface. Therefore, even as water and other non-sorbing solutes may be imbibed rapidly into dry aggregates, the pesticide will not penetrate far beyond the surface (in a short time-scale) due to its sorption to soil surfaces.

Although probably not statistically significant, there appeared to be a tendency for more rapid release of isoproturon from the air-dry aggregates after 24 h equilibration (Fig 1b) compared to the wetter aggregates. This is consistent with the moist aggregates permitting sorption-retarded diffusion into the aggregates, and so becoming less accessible to the bathing solution.

In order to help in identifying the controls on the release of pesticides from soil aggregates, it is useful to see if the curves given in Figs 1 to 4 can be represented using dispersion theory. The equation describing the release of a solute from a sphere originally at uniform concentration, C_0 , into a well-mixed solution (bathing water) initially free from the solute is given by Crank¹³ as

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1) \exp(-Dq_n^2 t/a^2)}{9+9\alpha+q_n^2 a^2} \quad (1)$$

where M_t is the total amount of solute (in this case radioisotope) in the solution at time t (hours), M_∞ is

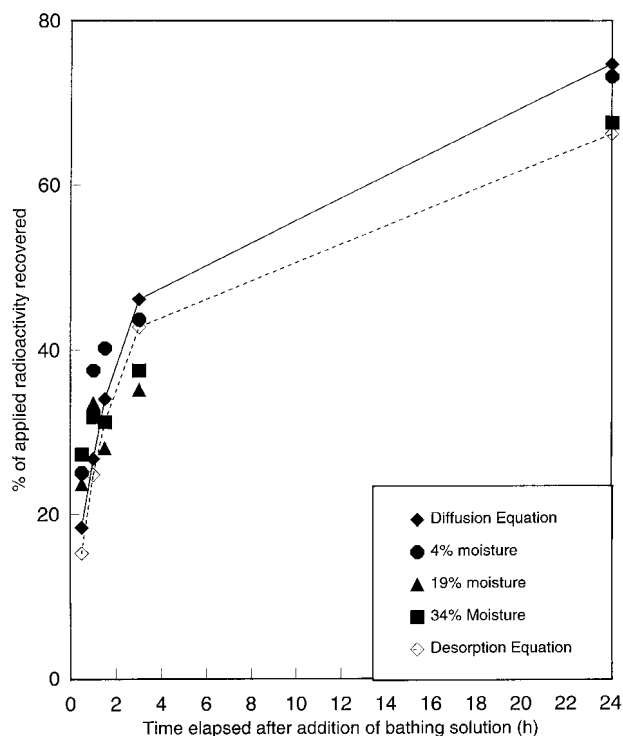


Figure 3. Recovery of [^{14}C]isoproturon from aggregates after 24 h incubation compared with that estimated using diffusion theory and non-equilibrium desorption approaches.

the corresponding quantity after infinite time, a is the radius of the sphere (mm) and D is the diffusion coefficient ($\text{mm}^2 \text{h}^{-1}$). The q_n s are the non-zero

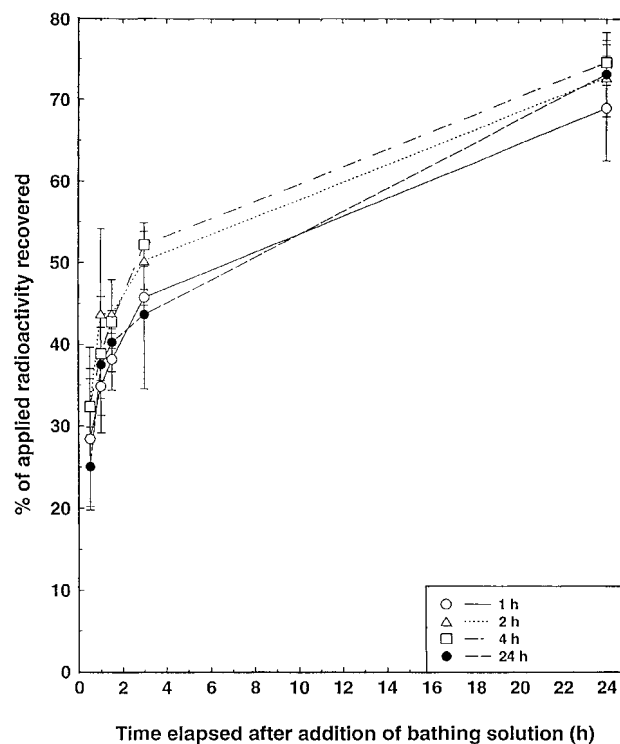


Figure 4. Recovery of [^{14}C]isoproturon from 4% moisture content aggregates after different equilibration periods (mean of three replicates with standard deviation shown).

solutions of

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \quad (2)$$

and $\alpha = 3V/(4\pi a^3)$, the ratio of the volumes of solution and sphere. The parameter α is expressed in terms of the final fractional uptake of the solute into the solution by the relation

$$\frac{3M_\infty}{4\pi a^3 C_0} = \frac{1}{1 + \left(\frac{1}{\alpha}\right)} \quad (3)$$

Where there is a preference of the solute for the solid or the solvent phase described by a partition factor K , then this is accommodated through modification of the parameter α , such that $\alpha = 3V/(4\pi a^3 K)$. Although in this sense, K is not strictly an equivalent to the equilibrium partition coefficient (K_d), a value of K equal to that of the K_d of isoproturon in soil from Wytham was used here.² In practice, the ability of the diffusion equations to predict the observed data was insensitive to the value of K , giving similar estimates with values of 1.5 and 3.5.

Before using the above equations here, it is important to consider the assumptions in their derivation against the conditions that existed in the experiments. Firstly it is assumed that the solvent is well mixed. In our experiments the bathing solution was swirled with the aggregates and then left undisturbed. In this case the solution was clearly well mixed at the beginning and then less so through time. However, the purpose of assuming the solution to be well mixed is to be able to say that the concentration in the solution is constant throughout the mixture. In this case it is not unreasonable to assume that diffusion of the solute, within a relatively small volume of solvent, might also achieve this constant concentration. In addition, the sampling of the solution will also have helped with the mixing.

A second assumption is that the aggregates are relatively spherical and that each of the aggregates is wholly in contact with the solvent, ie each aggregate acts as an independent sphere within the solution. Thirdly, the equations given here assume that the solute is initially evenly distributed through the sphere. The previous discussion has indicated that this is unlikely to be true in all cases and that there are particular differences between the distributions of isoproturon and tritiated water within the aggregates.

The derivation of eqn 1 assumes that the volume of the solution remains constant through time. In this case the liquid is sampled to calculate the amount of radioactivity in the solution phase and thus the volume decreases. This effect has been introduced into the equations by recalculating both the volumes after each sampling interval and the value of the equation parameters that depend on volume, namely M_∞ and α . This allows an approximation of the diffusion under the new driving forces for each of the periods between

sampling times. The amount of radioactivity removed in each sample is accounted for in the calculation of the amount of radioactivity removed from the aggregate.

Figure 2 shows the observed and modelled release of $^3\text{H}_2\text{O}$ from the initially dry aggregates for the four incubation periods. It is clear that one calculated curve was able to describe the observed behaviour within the first 4 h after the addition of the bathing solution in all four of these experiments ($R^2=0.81$). In this case, the diffusion coefficient was used to fit the observed data and a value of $0.14\text{ mm}^2\text{ h}^{-1}$ was found. However, reference to Figs 1a and 1b clearly shows that this estimated curve would not match the observed values for either the 19% or 34% moisture aggregates in any of the incubation periods shown. There is clearly a difference in the $^3\text{H}_2\text{O}$ removal from the dry and wet aggregates. The suggestion discussed above, that the $^3\text{H}_2\text{O}$ water was imbibed more deeply into the dry aggregate, is supported by the ability of the diffusion theory to match the experimental observations. The $^3\text{H}_2\text{O}$ taken deep into the aggregates needed to diffuse through the aggregate in order to reach the bathing solution. For the previously wet aggregates the diffusion pathway was clearly very short.

The same diffusion model, including the modification for a sorbed solute, was used to try to describe the observed release of labelled isoproturon from the aggregates. The observed values (Fig 3) were very well predicted by this model ($R^2=0.87$) using a diffusion coefficient of $0.007\text{ mm}^2\text{ h}^{-1}$. The much smaller diffusion coefficient is consistent with the fact that isoproturon is a much larger molecule than $^3\text{H}_2\text{O}$. It would appear, therefore, that the observed isoproturon release pattern was consistent with diffusion of the molecule from the aggregates. However, the difference in the pattern of the $^3\text{H}_2\text{O}$ and the isoproturon releases under the different initial wetness conditions points to a difference in the initial distribution of these solutes on the aggregates, as discussed above.

It was reasonable to assume that $^3\text{H}_2\text{O}$ applied to the dry aggregates was imbibed into the aggregates and was reasonably uniformly distributed. Therefore, the diffusion model used here was adequate to describe the observed release. The initial distribution of $^3\text{H}_2\text{O}$ on the wet aggregates was less certain, but it is likely that it remained near the surface, and subsequent release was more rapid than would have been predicted by considering diffusion processes. The similarity of the release patterns for isoproturon for all the initial wetness conditions suggests that the isoproturon was retained at the surface of the aggregates following its initial application. Therefore, the ability of diffusion alone to describe isoproturon release maybe purely coincidental and that the real control is the kinetics of the desorption process.

The kinetics of the desorption process can be represented as a time-varying partition coefficient that has an initial value of infinity and a final value of the

equilibrium partition coefficient, K_d . Ascribing a sensible exponential function to represent the variability with time results in

$$K'(t) = \frac{K_d}{1 - \exp(-kt)} \quad (4)$$

where k is the rate constant for desorption. It can be shown from considering the partition of a solute between the dissolved and solid phases within a system that

$$M_t = \frac{VC_T}{1 + mK'(t)} \quad (5)$$

where C_T is the concentration of isoproturon in the whole aggregate/solute system ($\mu\text{g mm}^{-3}$) and m is the concentration of the solid phase ($\mu\text{g mm}^{-3}$). Again, in this approach it was necessary to recalculate V after each sample was taken. Figure 3 shows the result of applying this equation to the experimental system and the comparison with the observed release of isoproturon from the aggregates. It is clear that taking this approach also allows the observed behaviour to be reproduced to an acceptable degree ($R^2=0.86$). The rate coefficient for the desorption process that produced the best fit was 0.1 h^{-1} . The desorption behaviour observed in the experiments can therefore be adequately represented by considering the sorption kinetics assuming all the applied pesticide remains at the surface. The release of pesticides from soil aggregates will not be altered by the water content of the aggregates prior to application, since the majority of the pesticide is retained at the aggregate surface by adsorption.

Figure 4 illustrates the effect of increasing the amount of time allowed for equilibration between the applied isoproturon and the aggregates in terms of ease of release of the pesticide when the soil is subsequently bathed in the new water. Increasing the time allowed for equilibration, from 1 to 24 h, appeared to have no effect on the strength of sorption with the dry aggregates (Fig 4). However, with the wetter aggregates, increasing the exposure time did reduce the initial amount of pesticide released into the bathing solution, clearly shown with the 34% moisture content aggregates (Fig 5). This may be interpreted as an increase in the strength of sorption with time, a feature observed before with isoproturon.² Alternatively, the sorption strength does not increase, but in the cycle of sorption and desorption of the pesticide on the surface of the aggregates, diffusion of the aqueous phase pesticide into the aggregate is taking place. This would be consistent with the observation being related to aggregates containing 34% moisture content, but not with the air-dry aggregates. Thus, more pesticide may diffuse deeper within the aggregate with time. This does not contradict the earlier interpretation of pesticides remaining at the surface of the aggregates, but suggests that inward movement of pesticide into the aggregates is retarded, unlike water. Increasing the

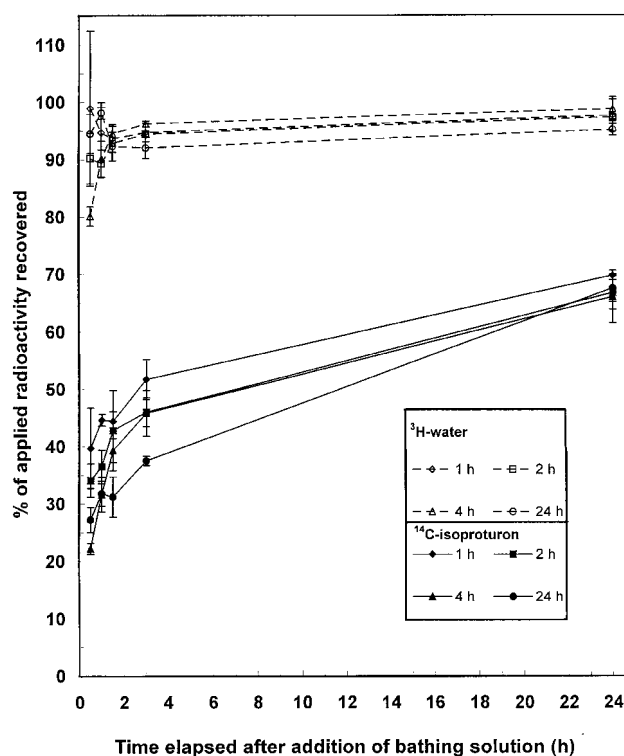


Figure 5. Recovery of $^3\text{H}_2\text{O}$ and ^{14}C isoproturon from 34% moisture content aggregates after different equilibration periods (mean of three replicates with standard deviation shown).

equilibration time did not affect the ease of release of $^3\text{H}_2\text{O}$ from the aggregates as shown by the data included in Fig 5.

4 CONCLUSIONS

- (1) Using both $^3\text{H}_2\text{O}$ and ^{14}C -labelled pesticide, with a scintillation counter that can differentiate between them, facilitates research into pesticide behaviour in a structured soil, particularly in increasing our understanding of how water and organic chemicals behave in soils with different antecedent moisture conditions.
- (2) Diffusion theory can adequately describe the release of $^3\text{H}_2\text{O}$ from the dry aggregates but not from those which were initially wet. This implies that the $^3\text{H}_2\text{O}$ was drawn into the dry aggregate to much greater extent than into the wet aggregates. The release of the ^{14}C -isoproturon was modelled adequately by considering either diffusion or non-equilibrium desorption as the main control. However, the lack of any difference in the release characteristics between the dry and wet aggregates would imply that the diffusion representation was fortuitous and that the real control on its release was the kinetics of the desorption process.
- (3) In soils with aggregates at intermediate and saturated moisture contents, the delay between pesticide application and the first storm event

reduces the amount of compound available for immediate transport. This is probably due to diffusion into the moist aggregates.

- (4) Isoproturon does not follow water convecting into dry soil aggregates. As with moist soil aggregates, the pesticide is prevented from moving rapidly into micropores within aggregates due to its sorption. There are sufficient sorption sites on the aggregate surface (within the topsoil) to retard isoproturon movement. Unlike the aggregates with a higher moisture content, with the air-dry aggregates the amount of pesticide available for transport did not reduce over a 24-h equilibration period.
- (5) This paper has indicated the relative importance of physical and chemical controls on the movement of isoproturon into and out of 2-mm soil aggregates. These controls will be a function of the sorption coefficient of the pesticide/soil combination and the size of the soil aggregate. The methods presented here could equally well be used in future research aimed at describing the controls under just such a range of circumstances.

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